

(19) Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) EP 0 992 538 B1

(12) EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
29.01.2003 Bulletin 2003/05

(51) Int Cl.: C08L 23/02, C08L 51/00,
C08L 23/22
// (C08L23/02, 23:22),
(C08L23/02, 51:00),
(C08L23/22, 23:02),
(C08L51/00, 23:02)

(21) Application number: 99115891.6

(22) Date of filing: 12.08.1999

(54) Star-branched rubber thermoplastic elastomer vulcanizates

Thermoplastische Elastomer Vulkanisate enthaltend ein sternförmig verzweigter Kautschuk

Vulcanisats d'élastomères thermoplastiques comprenant un caoutchouc ramifié en étoile

(84) Designated Contracting States:
DE ES FR GB IT NL

• Wang, Donald S. T.
Akron, Ohio 44321 (US)
• Schacht, Paul A.
Akron, Ohio 44313 (US)

(30) Priority: 27.08.1998 US 141223

(74) Representative:
Weber, Thomas, Dr.Dipl.-Chem. et al
Patentanwälte
von Kreisler-Selting-Werner,
Postfach 10 22 41
50462 Köln (DE)

(43) Date of publication of application:
12.04.2000 Bulletin 2000/15

(56) References cited:
EP-A- 0 320 263 EP-A- 0 448 902
EP-A- 0 678 529 GB-A- 875 947

(73) Proprietor: Advanced Elastomer Systems, L.P.
Akron, Ohio 44311-1059 (US)

(72) Inventors:
• Ouhadi, Trazollah
4020 Liege (BE)

EP 0 992 538 B1

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Description**Field of the invention**

5 [0001] The present invention relates to a curable composition comprising a thermoplastic polyolefin resin and a curable star-branched rubber, a thermoplastic elastomeric vulcanizate obtainable therefrom by dynamically vulcanizing said curable composition in the presence of suitable curative. The invention further relates to shaped articles comprising said vulcanizate.

Background/Prior art

10 [0002] Polymer blends which have a combination of both, thermoplastic and elastic properties (thermoplastic elastomers, TPE) are generally obtained by blending a thermoplastic polyolefin with an elastomeric composition (rubber) in a way such that the elastomer is intimately and uniformly dispersed as a discrete particulate phase within a continuous phase of the thermoplastic. Early work with vulcanized compositions is found in United States Patent 3,037,954 to Gessler which discloses static vulcanization as well as the technique of dynamic vulcanization wherein a vulcanizable elastomer is dispersed into a resinous thermoplastic polymer and the elastomer is cured while continuously mixing and shearing the polymer blend. The resulting composition (thermoplastic elastomer vulcanizate "TPV") is a microgel dispersion of cured elastomer, such as butyl rubber, chlorinated butyl rubber, polybutadiene or polyisobutene in an uncured matrix of thermoplastic polymer such as polypropylene. Since then the technology has advanced significantly.

15 [0003] United States Patent 3,037,954 discloses compositions comprising polypropylene and a rubber such as, inter alia, butyl rubber, chlorinated butyl rubber, polybutadiene, polychloroprene and polyisobutene.

20 [0004] United States Patents 3,758,643 and 3,806,558 disclose polymer blends comprising an olefin thermoplastic resin and an olefin copolymer rubber wherein the rubber is dynamically cured to a partial cure state. The compositions can be reprocessed, however, the potential applications of such blends are limited by their high compression set and/or low softening temperature resulting from only a partial cure of the rubber. Furthermore, the partial peroxide cure utilized in such blends is difficult to control from the standpoint of completeness of reaction, resulting in batch to batch variations in product properties.

25 [0005] Japanese Patent Application 85,530/87 discloses a DVA composition including a crystalline polypropylene as a matrix and two elastomers: a bromobutyl rubber and an olefin copolymer rubber such as EPM or EPDM rubber.

30 [0006] United States Patent 4,130,5334 discloses elastoplastic compositions comprising blends of cross-linked butyl rubber and a thermoplastic polyolefin resin. The blends disclosed comprise 20 to 45 parts by weight of the thermoplastic crystalline polyolefin resin and from 80 to 55 parts by weight of butyl rubber, chlorobutyl rubber or bromobutyl rubber, per 100 weight parts of polyolefin and rubber.

35 [0007] United States Patent 4,810,752 discloses a thermoplastic elastomer composition comprising a halobutyl rubber which is cured in the presence of a mixture of a polyolefin and a thermoplastic elastomeric block copolymer such as SIS, SEBS or SBS.

40 [0008] United States Patent 4,916,180 discloses a thermoplastic elastomer composition comprising a butyl terpolymer rubber and polypropylene. The rubber is cured with a peroxide curing agent. Said butyl terpolymer comprises a major portion of isobutylene, a major portion of isoprene and a minor portion of a divinyl aromatic monomer of the formula R-CR=CR-X-CR=CR-R in which X is an aromatic nucleus and R is independently selected from hydrogen or C₁₋₅ alkyl.

45 [0009] European patent application 0 320 263 (published on 14 June 1989) discloses the introduction of branching into C₄ to C₇ isoolefin homopolymer rubber, butyl copolymer rubber, halogenated copolymer rubber (C₄ to C₇ isoolefin/ C₄ to C₁₄-conjugated diene), and mixtures thereof by reaction with a functional agent, i.e., a branching agent for the purpose of modifying the molecular weight distribution. The modification of the molecular weight distribution of said rubbers is achieved by incorporating during polymerization of the polymers an effective amount of a functional reagent selected from the group consisting of polymers and copolymers comprising functional groups capable of copolymerizing or forming a chemical bond with the product polymer, the functional group comprising cationically active halogen or cationically active unsaturation and such polymers and copolymers preferably comprising lyophilic polymerization diluent soluble moiety. The copolymers thus obtained are called "star-branched copolymer rubbers" or "star-branched butyl rubbers" and may be halogenated.

50 [0010] United States Patent 5,286,804 and the International Patent Application Publication WO 91/13102 disclose an improved process for halogenating star-branched butyl rubbers.

55 [0011] The thermoplastic elastomer vulcanizates based on butyl and halogenated butyl rubbers known in the art, however, show limitations with respect to the balance of physical properties (tensile strength, elongation at break) and processability, i.e., allowing to obtain shaped articles after injection-molding, extrusion and blow-molding which show no defect, such as on the surface, at the edges. Also the manufacturing process of these butyl and halogenated butyl

rubber based thermoplastic elastomers has been found to be difficult and complicated and requires intensive mixing.

[0012] It is an object of the present invention to provide curable composition which comprises a thermoplastic polyolefin resin and a rubber which can be converted into a thermoplastic elastomer vulcanizate which has an improved balance of physical properties and superior processability. In detail it is an object of the present invention to provide a thermoplastic elastomer based on not only butyl but also halogenated derivatives which is easy to be manufactured and easy to be processed using all the processing devices like extrusion, injection molding, blow molding, with excellent articles aspects.

Description of the Invention

[0013] It has surprisingly been found that blends of a thermoplastic polyolefin resin and a curable star-branched rubber (copolymer) when dynamically cured in the presence of a suitable curative or curative system yields a better processability and the articles comprising the cured vulcanizate show a smoother surface (higher surface rating) compared to conventional butyl rubbers or halogenated butyl rubbers. The quality of extrusion which is a key parameter for the commercial success of a thermoplastic elastomer has been found to be improved significantly.

[0014] The thermoplastic elastomers of the present invention have the well-known functional properties inherent to conventional butyl rubber like impermeability, heat/flex resistance and damping equivalent to thermoplastic elastomers made with traditional butyl rubbers.

[0015] In detail, the present invention relates to a curable composition comprising a blend of

- (i) a thermoplastic polyolefin resin; and
- (ii) a curable star-branched rubber.

[0016] Furthermore, the present invention relates to a thermoplastic elastomer vulcanizate obtainable from the curable composition as defined above by dynamically curing the rubber in the presence of a suitable curative or curative system under conditions of shear at a temperature above the melting temperature of the thermoplastic component.

Thermoplastic polyolefin resin

[0017] Polyolefins suitable for use in the thermoplastic elastomer blends of the invention include thermoplastic, crystalline polyolefin homopolymers and copolymers. They are desirably prepared from monoolefin monomers having 2 to 7 carbon atoms, such as ethylene, propylene, 1-butene, isobutylene, 1-pentene, 1-hexene, 1-octene, 3-methyl-1-pentene, 4-methyl-1-pentene, 5-methyl-1-hexene, mixtures thereof and copolymers thereof with (meth)acrylates and/or vinyl acetates. Preferred, however, are monomers having 3 to 6 carbon atoms, with propylene being most preferred.

[0018] As used in the specification and claims the term polypropylene (PP) includes homopolymers of propylene as well as reactor copolymers of polypropylene which can contain 1 to 40% by weight of ethylene or an α -olefin comonomer of 4 to 16 carbon atoms, and mixtures thereof. Random propylene copolymer with one or more co-monomers selected from ethylene or an α -olefin having 4 to 16 carbon atoms can be used alone or/and with other polypropylenes described above. The polypropylene can be highly crystalline isotactic or syndiotactic polypropylene. The polypropylene used for this invention can be made via either a Ziegler-Natta or single site catalysis system. Commercially available polyolefins may be used in the practice of the invention. Further polyolefins which can be used in terms of the invention are high, low, linear-low, very low density (including those made with single-site catalyst system) polyethylenes and copolymers of ethylene with (meth)acrylates and/or vinyl acetates.

Star-branched rubber

[0019] In the following "star-branched rubber" is used interchangeably with "star-branched copolymer" or "star-branched copolymer rubber". In the art star-branched rubbers are often called "star-branched butyl rubber" or "star-branched butyl".

[0020] Star-branched rubbers, the halogenation thereof, their methods of preparation and further technological background is disclosed in detail in European Patent Application EP-0 320 263, in Paper No. 21 entitled "Star-branched Butyl, A Novel Butyl Rubber For Improved Processability" presented at the Rubber Division of the American Chemical Society, Mexico City, Mexico, 9-12 May, 1989 by H.C. Wang and the references cited therein. Furthermore, reference is made to United States Patent 5,286,804 and the International Patent Application Publication WO 91/13102 and the references cited therein. The star-branched rubbers contain long branched structures by incorporating, during polymerization of the C₄ to C₁₄ multiolefin, an effective amount of a cationically functional reagent selected from the group consisting of polymers and copolymers comprising functional groups capable of copolymerizing or forming a chemical bond with the product polymer, the functional group comprising cationically active halogen or cationically active un-

EP 0 992 538 B1

saturation an such polymers and copolymers preferably comprising lyophilic polymerization diluent soluble moiety.

[0020] Classes of functional polymeric reagents which are useful for obtaining the star-branched rubbers are represented by the following formulae (I) to (III):

5



wherein

10

R_1 , R_2 and R_3 independently represent hydrogen or a C_1 to C_{15} , preferably C_1 to C_4 alkyl group,
 R_4 and R_5 independently represent a C_1 to C_{15} , preferably C_1 to C_4 alkylene group,
 X represents halogen, preferably chlorine or bromine,
 m represents an integer of 4 to 100.

15

Most preferred for the alkyl groups R_1 to R_3 are the methyl and ethyl group and for R_4 and R_5 the methylene and ethylene group.

[0021] Suitable reagents in this class include chlorinated butyl and brominated butyl.

20



wherein

25

R_6 represents a C_1 to C_{15} , preferably C_1 to C_4 alkyl or an aryl group containing up to 14, preferably up to 9 carbon atoms,
 R_4 , R_5 and X are as defined above in context with formula (I),
 n represents an integer of 4 to 100.

30

[0022] Most preferred aryl groups for R_1 are the phenyl or tolyl group.

[0023] Suitable reagents in this class include hydrochlorinated polyisoprene, hydrobrominated polyisoprene, iso-butylene-vinylbenzyl chloride copolymer and chlorinated polystyrene.

35



wherein

40 R_7 and R_8 independently represent hydrogen, a C_1 to C_{15} , preferably C_1 to C_4 alkyl, an aryl group containing up to 14, preferably up to 9 carbon atoms or an C_2 to C_4 alkenyl group,
 R_4 and R_5 are as defined above in context with formula (I),
 p represents an integer of 7 to 1,000.

[0024] The most preferred alkenyl groups for R_7 and R_8 are ethenyl and propenyl.

[0025] Suitable reagents in this class include polybutadiene, polyisoprene and polypiperylene.

45

[0026] More specifically, said cationically functional reagent comprising a cationically active unsaturation comprises a polydiene and partially hydrogenated polydiene selected from the group consisting of polybutadiene, polyisoprene, polypiperylene, natural rubber, styrene-butadiene rubber, ethylene-propylene diene monomer rubber, styrene-butadiene-styrene and styrene-isoprene-styrene block copolymers. More preferably said reagent further comprises a lyophilic polymerization diluent soluble portion. Examples comprise polystyrene comprising cationically active halogen functionality, or a hydrohalogenated styrene-isoprene-styrene triblock polymer, wherein said triblock polymer preferably has a number average molecular weight of from 100,000 to 300,000 the central polyisoprene block prior to hydrohalogenation comprises from 1 to 10 weight percent of said triblock polymer and following hydrohalogenation contains from 0.1 to 1.0 weight percent halogen.

50

[0027] The reactive branching agents for use in producing the star-branched polymers are present during polymerization of the isomonoolefin and the multiolefin monomers. Generally, such agents are present in an amount based on said monomers, greater than 0.3 weight percent, e.g., 0.3 to 3.0 weight percent, preferably greater than 0.35 weight percent, e.g., 0.35 to 2.8 weight percent, more preferably greater than 0.4 to 2.7 weight percent, e.g., 0.45 to 2.6 weight

percent, for example greater than 0.5 weight, e.g., 0.5 to 5.0 weight percent. Reagents which are not excessively reactive can be used in a commercial process, at e.g., 1.1 to 2.0 weight percent. The star-branched rubber may be further halogenated as described in United States Patent 5,286,804 or the International Patent Application Publication WO 91/13102 and may contain chemically bound chlorine, bromine or iodine. The rubber may comprise from 0.05 to

5 5 weight percent of chemically bound halogen. When the halogen is chlorine, the preferred amount of chemically bound chlorine ranges from 0.1 to 2.0 weight percent. When the halogen is bromine, the preferred amount of chemically bound bromine ranges from 0.2 to 4.0 weight percent.

[0028] The star-branched rubber contains less than 30% by weight of the conjugated multiolefin based on the total amount of isomonoolefin and conjugated multiolefin. Preferably star-branched rubber comprises 85 to 99.5% by weight of the C₄ to C₇ isomonoolefin and 15 to 0.5% by weight of the multiolefin, based on the amount of the isomonoolefin and multiolefin (feed blend). A preferred C₄ to C₇ isomonoolefin is isobutylene, preferred C₄ to C₁₄ multiolefins are selected from isoprene, butadiene, dimethylbutadiene and piperylene. Instead of the C₄ to C₁₄ multiolefins para-C₁ to C₄-alkyl styrene or, preferably its halogenated derivative containing 0.1 to 10% by weight of halogen such as chlorine or bromine can be used as well.

[0029] The blend comprising the thermoplastic polyolefin resin (i) and the curable star-branched rubber (ii) comprises 15 to 80 % by weight, preferably 18 to 65 % by weight, more preferably 22 to 55 % by weight of the thermoplastic polyolefin resin (i) and 85 to 20 % by weight, preferably 82 to 35 % by weight, more preferably 78 to 45 % by weight of the curable star-branched rubber (ii), based on the amount of (i) and (ii). The same amounts are true for the vulcanizate in which the curable star-branched rubber has partially or fully been cured by a suitable curative or curative system as described below.

Additives:

[0030] In addition to its polymer component, i.e., the thermoplastic polyolefin resin and the star-branched rubber the thermoplastic elastomer vulcanizate (TPV) composition of this invention may include as an additive reinforcing and non-reinforcing fillers, antioxidants, stabilizers, rubber processing oils, rubber/thermoplastic phase compatibilizing agents, lubricants (e.g., oleamide), antiblocking agents, antistatic agents, waxes, coupling agents for the fillers and/or pigment, foaming agents, pigments, flame retardants, and other processing aids known to the rubber compounding art. The pigments and fillers can comprise up to 50 wt% of the total vulcanized composition, based on polymer components and additives, preferably pigments and fillers comprise about up to 40 wt% of the total composition. The total amount of additives, including pigments and fillers, may be up to 70 wt%, based on the total composition.

[0031] Fillers can be inorganic fillers such as calcium carbonate, clays, silica, talc, titanium dioxide or carbon black. Any type of carbon black can be used, such as channel blacks, furnace blacks, thermal blacks, acetylene black and lamp black.

[0032] Rubber process oils have particular ASTM designations depending on whether they fall into the class of paraffinic, naphthenic or aromatic process oils. They are derived from petroleum fractions. The type of process oil utilized will be that customarily used in conjunction with the rubber component. The ordinarily skilled rubber chemist will recognize which type of oil should be utilized with a particular rubber. The quantity of rubber process oil utilized is based on the total rubber content, both cured and uncured, and can be defined as the ratio, by weight, of process oil to the total rubber in the TPV. This ratio can vary from 0 to 4/1; preferably 0.4/1 to 3.5/1; more preferably 0.8/1 to 3.2/1. Larger amounts of process oil can be used, the resultant effect being reduced physical strength of the composition. Oils other than petroleum based oils, such as oils derived from coal tar and pine tar, can also be utilized. In addition to the petroleum derived rubber process oils, organic esters and other synthetic plasticizers can be used. Furthermore, the low molecular weight synthetic polyolefins like α-olefinic process oil, low molecular weight polybutene, can be used as process oil.

[0033] The ratio of the process oil defined above includes the extending oil which may be contained in rubber plus additional oil added during the manufacture of the thermoplastic elastomer.

[0034] Antioxidants can be utilized in the composition of this invention. The particular antioxidant utilized will depend on the rubbers utilized and more than one type may be required. Their proper selection is well within the ordinary skill of the rubber and thermoplastic processing chemist. Antioxidants will generally fall into the class of chemical protectors or physical protectors.

[0035] Physical protectors are used where there is to be little movement in the part to be manufactured from the composition. The physical antioxidants include mixed petroleum waxes and microcrystalline waxes. These generally waxy materials impart a "bloom" to the surface of the rubber part and form a protective coating to shield the part from oxygen, ozone.

The chemical protectors generally fall into three chemical groups; secondary amines, phenolics and phosphites. Illustrative, non-limiting examples of types of antioxidants useful in the practice of this invention are hindered phenols, amino phenols, hydroquinones, alkyldiamines, amine condensation products. Further examples of these and other

types of antioxidants are styrenated phenol; 2,2'-methylene-bis-(4-methyl-6-t-butylphenol); 2,6'-di-t-butyl-o-dimethylamino-p-cresol; hydroquinone monobenzyl ether, octylated diphenyl amine; phenyl-beta-naphthylamine; N,N'-diphenylethylene diamine; aldol-alpha-naphthylamine; N,N'-diphenyl-p-phenylene diamine.

5 Curing system:

- [0036] The composition of the invention, the rubber component of the TPV will be partially or fully vulcanized/crosslinked. Those of ordinary skill in the art will appreciate the appropriate quantities, types of cure systems and vulcanization conditions required to carry out the partial or full vulcanization of the rubber. The rubber can be vulcanized using varying amounts of curative, varying temperatures and varying time of cure in order to obtain the optimum partial or full crosslinking desired. Any known cure system can be used, so long as it is suitable under the vulcanization conditions for the rubber being used and is compatible with the thermoplastic polyolefin resin component of the TPV. These curatives include sulfur, sulfur donors, metal oxides, resin systems and high energy radiation both with and without accelerators and co-agents.
- [0037] Organic peroxides with an adequate well-known co-agent can be used as cure system except where the butyl rubber is a non-halogenated butyl rubber. The role of the co-agent in peroxide cure systems is to enhance the cure-state and inhibiting chain-fragmentation or scission effect. Specific examples of useful organic peroxides are selected from octanoyl peroxide, lauroyl peroxide, benzoyl peroxide, tert.-butyl peroxyoctoate, p-chlorobenzoyl peroxide, 2,4-dichlorobenzoyl peroxide, cyclohexanone peroxide, tert.-butyl peroxybenzoate, methyl ethyl ketone peroxide, dicumyl peroxide, di-tert.-butyl peroxide, 2,5-dimethyl-2,5-di(benzoylperoxy)hexane 2,5-dimethyl-2,5-di(tert.-butylperoxy)hexane, di-tert.-butyl diper oxyphthalate, tert.-butylcumyl peroxide, diisopropylbenzene hydroperoxide, 1,3-bis(tert.-butylperoxyisopropyl)benzene tert.-butyl peroxy-pivalate, 3,5,5-trimethylhexanoyl peroxide, 1,1-bis(tert.-butylperoxy)-3,5,5-trimethylcyclohexane, 1,1-bis(tert.-butylperoxy)cyclohexane; azo compounds such as azobisisobutyronitrile.
- [0038] The peroxide-based cure systems may be used with or without co-agents such as ethylene dimethacrylate, polyethylene glycol dimethacrylate, trimethylol propane trimethacrylate, divinyl benzene, diallyl itaconate, triallyl cyanurate, diallyl phthalate, allyl methacrylate, cyclohexyl methacrylate, and m-phenylene bis maleimide (NVA-2).
- [0039] Phenolic resin curatives are preferred for the preparation of the thermoplastic elastomer vulcanizate of the invention, and such cure systems are well known in the art and literature of vulcanization of rubbers. Their use in vulcanized compositions is more fully described in United States Patent 4,311,628.
- [0040] A basic ingredient of such system is a phenolic curing resin made by condensation of halogen substituted phenol, C₁-C₁₀ alkyl substituted phenol or unsubstituted phenol with an aldehyde, preferably, formaldehyde, in an alkaline medium or by condensation of bifunctional phenoldialcohols. Dimethylol phenols substituted in the para-position with C₅-C₁₀ alkyl groups are preferred. Halogenated alkyl substituted phenol curing resins prepared by halogenation of alkyl substituted phenol curing resin are also especially suitable. Phenolic curative systems comprising methylol phenolic resins, halogen donor and metal compound are especially recommended, details of which are described in Giller, United States Patents 3,287,440 and Gerstn et al, 3,709,840. Non-halogenated phenol curing resins are used in conjunction with halogen donors, preferably, along with a hydrogen halide scavenger. Ordinarily, halogenated, preferably brominated, phenolic resins containing 2-10 weight percent bromine, do not require halogen donor but are used in conjunction with a hydrogen halide scavenger such as metal oxides such as iron oxide, titanium oxide, magnesium oxide, magnesium silicate, silicon dioxide and preferably zinc oxide, the presence of which promotes the cross-linking function of the phenolic resin, however, with rubbers which do not readily cure with phenolic resins, the conjoint use of a halogen donor and zinc oxide is recommended. The preparation of halogenated phenol resins and their use in a curative system with zinc oxide are described in United States Patents 2,972,600 and 3,093,613. Examples of suitable halogen donors are stannous chloride, ferric chloride, or halogen donating polymers such as chlorinated paraffin, chlorinated polyethylene, chlorosulfonated polyethylene, and polychlorobutadiene (neoprene rubber). The term "activator" as used herein means any material which materially increases the cross-linking efficiency of the phenolic curing resin and includes metal oxides and halogen donors either used alone or conjointly. For further details of phenolic curative systems see "Vulcanization and Vulcanizing Agents," W. Hoffman, Palmerton Publishing Company. Suitable phenolic curing resins and brominated phenolic curing resins are commercially available, for example, such resins may be purchased under the trade names SP-1045, CRJ-352, SP-1055 and SP-1056 from Schenectady Chemicals, Inc. Similar functionally equivalent phenolic curing resins may be obtained from other suppliers. As explained above, sufficient quantities of curatives are used to achieve essentially complete cure of the rubber.
- [0041] For halogenated butyl rubbers, a preferred cure system is one which is based on ZnO and/or MgO. In this system, the MgO does not act as an activator but as an acid acceptor to stabilize the rubber from dehydrohalogenation.
- [0042] Another preferred cure system for halogenated butyl rubbers comprises ZnO and a maleimide product. Among the maleimide product, a bismaleimide is especially superior in effectiveness and m-phenylene bismaleimide (4,4'-m-phenylene bismaleimide) (HVA-2) preferred. Other examples of the bismaleimide are 4,4'-vinylenediphenyl bismaleimide, p-phenylene bismaleimide, 4,4'-sulfonyldiphenyl bismaleimide, 2,2'-dithiodiphenyl bismaleimide, 4,4'-ethylene-

bis-oxophenyl bismaleimide, 3,3'-dichloro-4,4'-biphenyl bismaleimide, o-phenylene bismaleimide, hexamethylene bis-maleimide and 3,6-durine bismaleimides.

[0043] Usually 1 to 15 weight parts of the curative or curative system are used per 100 weight parts of the rubber to be cured.

5

General procedure:

[0044] The rubber component of the thermoplastic elastomer vulcanizate is generally present as small, i.e., micro-size, particles within a continuous polyolefin resin matrix, although a co-continuous morphology is also possible depending on the amount of rubber relative to plastic with or without rubber curing, and the cure system or if the rubber is cured, the degree of cure of the rubber. The rubber is partially or fully crosslinked/cured, preferably the rubber is fully crosslinked.

10

[0045] The full crosslinking can be achieved by adding an appropriate rubber curative or curative system to the blend of thermoplastic polyolefin resin and the rubber and vulcanizing the rubber to the desired degree under conventional vulcanizing conditions. However, it is preferred that the rubber be crosslinked by the process of dynamic vulcanization. As used in the specification and claims, the term "dynamic vulcanization" means a vulcanization or curing process for a rubber contained in a thermoplastic elastomer composition, wherein the curable rubber is vulcanized under conditions of high shear at a temperature above the melting point of the thermoplastic polyolefin component. The rubber is thus simultaneously crosslinked and dispersed as fine particles within the polyolefin matrix, although as noted above, other morphologies may also exist. Dynamic vulcanization is effected by mixing the thermoplastic elastomer components at elevated temperature in the presence of a rubber curative in conventional mixing equipment such as roll mills, Banbury mixers, Brabender mixers, continuous mixers, mixing extruders such as single and twin-screw extruders. Thereby the dynamically partially or fully vulcanized rubber/plastic alloy is obtained. The unique characteristic of dynamically cured compositions is that, notwithstanding the fact that the rubber component is preferably fully cured, the compositions can be processed and reprocessed by conventional plastic processing techniques such as extrusion, injection molding and compression molding. Scrap or flashing can be salvaged and reprocessed.

20

[0046] Preferably, after the thermoplastic terpolymer and rubber are intimately mixed, the curative is added. Heating and masticating at vulcanization temperatures are generally adequate to complete the vulcanization reaction in a few minutes or less, but if shorter vulcanization times are desired, higher temperatures may be used. A suitable range of vulcanization temperature is from about the melting temperature of the thermoplastic terpolymer, i.e., between 120°C to about 250°C or more. Typically, the range is from 150°C to 225°C. A preferred range of vulcanization temperatures is from 180°C to 220°C. To obtain thermoplastic elastomer vulcanizates, it is important that mixing continues without interruption until vulcanization occurs. Mixing is continued until a maximum mixing torque indicates that vulcanization has occurred. The vulcanized composition is then removed from the mixer. The vulcanized composition then can further be processed as mentioned above.

25

[0047] The term "partially vulcanized" as used herein means that not all of the rubber component capable of being cured has been cured. The term "fully vulcanized" as used herein means that the rubber component to be vulcanized has been cured to a state in which the elastomeric properties of the crosslinked rubber are similar to those of the rubber in its conventional vulcanized state, apart from the thermoplastic elastomer composition. Simply stated, fully vulcanized means that all of the rubber component which is capable of being vulcanized, has been vulcanized (cured). The degree of cure can be described in terms of gel content or conversely, extractable components. Alternatively the degree of cure may be expressed in terms of crosslink density. All of these descriptions are well known in the art, for example from U.S. Patent 5,100,947 and U.S. Patent 5,157,081.

30

[0048] The modified thermoplastic elastomer vulcanizate of the present invention is used in processes for making shaped articles by conventional processing such as co-injection, co-extrusion, blow-molding, co-blow-molding (injection and extrusion), lamination, calendering, overmolding by injection and compression, and over-extrusion.

35

[0049] The invention will be better understood by reference to the following examples.

40

[0050] Unless otherwise indicated throughout this invention weight parts or % by weight are used to characterize the compositions.

45

Examples:

[0051] The following compounds were used in the experiments:

50

Exxon Butyl 268:

conventional isoprene-isobutylene rubber, 46-55
Mooney viscosity (1 + 8)125 °C from Exxon Chemical;

EP 0 992 538 B1

Exxon SB Butyl 4268 and MDB 90/4:

star-branched butyl rubber, copolymer of isobutylene and isoprene, including a styrene-butadiene rubber (SBR) copolymer branching agent, available from Exxon Chemical under Grade 4268 and MDB 90/4, respectively with 34-44 and Mooney viscosity 40 (1 + 8) 125 °C;

Exxon SB Chlorobutyl 5066 and MDB 88/4:

chlorinated star-branched butyl rubbers, chlorinated copolymer of isobutylene and isoprene, including a styrene-butadiene rubber (SBR) copolymer branching agent, available from Exxon Chemical under Grade 5066 and MDB 88/4, respectively with 35-45 and 40 Mooney viscosity (1 + 8) 125 °C;

Exxon SB Bromobutyl 6255 Rubber:

brominated star-branched butyl rubber, brominated copolymer of isobutylene and isoprene, including a styrene-butadiene rubber (SBR) copolymer branching agent, available from Exxon Chemical under Grade 6255 with 41-51 Mooney viscosity (1 + 8) 125 °C;

Exxon bromobutyl 2244 Rubber: brominated isoprene-isobutylene rubber, 41-51 Mooney viscosity (1 + 8) 125 °C; Aristech TI 4007 G Polypropylene: polypropylene reactor copolymer, MFI = 0.75 (dg/min., 230 °C) from Aristech;

Exxon PP 7032 Polypropylene: reactor polypropylene copolymer, MFI = 4 (dg/min., 230 °C) from Exxon Chemical;

Lyondell 51507A Polypropylene: homo polypropylene from Lyondell;

Aristech D 00814 Polypropylene: homo polypropylene from Aristech;

Exxon Escorez 5320 Hydrocarbon: synthetic hydrocarbon resin from Exxon Chemical;

Translink 37 Clay: calcinated and surface modified kaolin from KMG Mineral, Inc.;

Maglite D MgO: Magnesium oxide from C.P. HALL Co.;

Stearic Add F 100: long chain fatty acid (any source);

Irganox 3114: tris(3,5-di-tert.-butyl-4-hydroxybenzyl) isocyanurate antioxidant from CIBA-Geigy;

Ultranox 626: bis(2,4-di-t-butylphenyl)pentarylthritol phosphite from Borg Warner;

Exxon Chlorobutyl 1068: chlorinated isoprene-isobutylene, 33-43 Mooney viscosity (1 + 8) 125 °C;

Exxon Parapol 950: low molecular weight polyisobutylene from Exxon Chemical (viscosity: 193-247 cSt at 100 °C);

ZnO: zinc oxide (any source);

Aristech FP 200F Polypropylene: homo polypropylene, MFI = 20 (dg/min., 230 °C);

Exxon Vistalon 808: ethylene-propylene copolymer rubber, 77 wt.% ethylene, Mooney viscosity (1 + 8) 125 °C from Exxon Chemical;

HVA-2: N,N-m-phenylene dimaleimide: from Du Pont;

Lyondell Arco Prime 350 White Oil: extracted paraffinic process oil from Lyondell;

Icecap K Clay: aluminum silicate from Burgess Pigment;

Pro Flow 100: LMWPP, available from Poly Visions, Inc.;

Rexene FDO D 100: homo-polypropylene, MFI = 14 (dg/min., 230 °C) from Rexene;

Optema TC 140: ethylene methylacrylate copolymer, 21.5% methylacrylate, MFI = 135 (ASTM D-1238) from Exxon Chemical;

SnCl₂: tin chloride monohydrate (any source);

SP-1045: alkyl phenol formaldehyde from Schenectady;

Sunpar 150 M: mineral paraffinic process oil from Sun Oil Company;

DC-200 (Food Grade): dimethyl polysiloxane with 350 cSt viscosity from Dow Corning;

Plasthall 4141: triethylene glycol caprate-caprylate available from C.P. Hall Company;

Kemamide U: oleamide from Humko Chemical Division;

Kemamide S: stearamide from Humko Chemical Division;

CB 1068: chlorinated butyl rubber, chlorinated copolymer of isobutylene and iso-prene available from Exxon Chemical with 35-45 Mooney viscosity (1 + 8) 125 °C

PPH 1050: homo polypropylene, MFI = 0.3 (dg/min) from Hoechst;

Neutral 600: extracted paraffinic oil from Exxon Chemical;

SRF 762: carbon black from Cabot;

HVA-2: N,N-m-phenylene dimaleimide from Du Pont;

Unislip 1757: fatty acid-amide from Unichema;

Vistalon 808: ethylene-propylene copolymer rubber, 77 wt.% ethylene, Mooney viscosity (1 + 8) 125 °C from Exxon Chemical;

EP 0 992 538 B1

[0052] The following measurement methods (standards) were used:

Hardness (Shore A): ISO 868-85 or ASTM D2240
 5 Elongation at break (EB): DIN 53504 or ASTM D412
 Ultimate tensile strength (UTS): DIN 53504 or ASTM D412
 Mod. 100: Modulus at 100% elongation: DIN 53504 or ASTM D412
 Tension set: ASTM D412
 ACR viscosity: Automatic Capillary Rheometer is a test method according to TPE-0137
 10 (Advanced Elastomer Systems internal test) similar to ASTM-3835-93a. This test is operating at constant shear stress at 204 °C using a die with L/D = 0.031.
 Extrusion Surface Rating: Test method according to TPE-0106 (Advanced Elastomer Systems internal test), similar to ANSI (American National Standards Institute) B 46.1
 15 "Surface Texture ...". The product to be evaluated is extruded into strips under standard conditions: A 2.54 cm or 3.81 cm diameter extruder, equipped with a 24:1 L/D screw having a 3-3.5 compression ratio is used. The extruder is fitted with a strip die 25.4 mm wide x 0.5 mm thick x 7-10 mm land length. Breaker plate is used with the die.
 Temperature set is: 180 °C (feed zone), 190 °C, 200 °C, 205 °C (die zone).

The surface smoothness of the extruded strip is measured with a stylus profilometer. The arithmetic average of the surface irregularity (R_a) is used to qualify surface smoothness.

20 The smaller the value, the better the surface smoothness.

Tear strength: ASTM D624 die C

Compression set: ISO 815 type B

Mod. 300: Modulus at 300 %

elongation: DIN 53504 or ASTM D412

25

Experimentation:

[0053] A thermoplastic vulcanizate (TPV) can be made by dynamically curing a star branched butyl rubber (SBB) or star branched halogenated butyl rubber in the presence of the melted polypropylene plastic. The product offers im-

30 proved processability (lower viscosity & smoother surface finishing) versus regular butyl/PP TPV. Table 1 shows a comparison property of the SB-butyl (4268)/PP TPV with the regular butyl (268)/PP TPV in an SP-1045 cured system. It is found that the ACR viscosity has significantly been reduced and the Extrusion Surface Rating (ESR) properties have been drastically improved (reduced) when the rubber phase is a star branched butyl rubber in comparison to a normal butyl rubber. In another series of experiments using star branched butyl rubber (Br-SBB) (6255) versus traditional butyl rubber with HVA-2 as cure system, the same trend has been found as shown in Table 2. In these experiments, different PP's have been evaluated with both types of butyl rubbers.

[0054] The rheology-property of the SBB-TPV (shear viscosity) were also found to be improved as is evident from the following data:

40

VISCOSITY vs. SHEAR RATE				
Apparent Viscosity, Pa·s (poise)				
Apparent Shear Rate	18 s ⁻¹	82 s ⁻¹	387 s ⁻¹	1800 s ⁻¹
Sample 1*	2383.5 (23835)	815.8 (8158)	274.7 (2747)	91.7 (917)
Sample 2*	1977.8 (19778)	716.6 (7166)	251.2 (2512)	86.2 (862)
Sample 3*	2129.9 (21299)	749.7 (7497)	258.3 (2583)	89.7 (897)
Sample 4*	1572.1 (15721)	617.4 (6174)	220.7 (2207)	78.1 (781)

45

* see Table 1 below

[0055] The experimental result is further illustrated by Figure 1.

50

Table 1: Star-Branched Butyl Rubber/PP TPVs

Sample	1	2	3	4	5	6	7	8
Ingredients	wt.%	wt.%						
Exxon Butyl 268	54.67	54.67	54.67	54.67	54.67	40.72	40.72	40.72
Exxon SB Butyl 4268 Rubber	54.67					40.72		40.72
Icerap K Clay	5.47	5.47	5.47	5.47	5.47	4.07	4.07	4.07
Exxon PP7032 (Copo, 4 MFI)	5.47	5.47	8.20	8.20	16.29	16.29	16.29	16.29
ProFlow 1000 (LHMWPP)	5.47	5.47	8.20	8.20				
Rexene FPO D100 (Homo- PP, 14 MFI)	5.47	5.47			4.07	4.07	40.07	4.07
Oplama TC140 (E/MA, 21.5% MA, 135 MFI)	10.93	10.83	10.93	8.14	8.14	8.14	8.14	8.14
ZnO	1.09	1.09	1.09	0.81	0.81	0.81	0.81	0.81
SiO ₂	0.71	0.71	0.71	0.53	0.53	0.53	0.53	0.53
SP-1045	2.73	2.73	2.73	2.04	2.04	2.04	2.04	2.04
Sunpar 150M				18.32	18.32			
DC-200 (Food Grade, 350 cst.)	3.99	3.99	3.99					
Plastiball 4141 (Tributylene Glycol Caprate-Caprylate)						18.32	18.32	
Kemamide U	3.99	3.99	3.99					
Kemamide S				5.01	5.01	5.01	5.01	
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	

Table 1 (continued)

Room Temperature Property

Sample	1	2	3	4	5	6	7	8
Specific Gravity (g/cm ³)	0.96	0.96	0.97	0.97	0.94	0.94	0.95	0.96
Hardness A, 5 sec.	67	58	70	63	71	64	63	64
EB, %	430	288	270	260	460	410	120	130
UTS, MPa (psi)	4.62 (670)	3.10 (450)	4.34 (630)	3.65 (530)	4.89 (710)	4.68 (680)	4.48 (650)	3.65 (530)
Mod. 100, MPa (psi)	2.07 (300)	2.34 (340)	2.89 (420)	2.86 (430)	2.27 (330)	3.10 (450)	3.93 (570)	3.10 (450)
Tension Set, %	16	25	25	31	23	29	32	37
A.C.R. viscosity, Pa·s (poise)								
204°C, 0.35 MPa (51 psi)	330 (3300)	190 (1900)	220 (2200)	140 (1400)	46 (460)	36 (360)	21 (210)	14 (140)
Extrusion Surface Rating	116	53	82	37	101	45	87	61

Table 2: Star-Branched Butyl Rubber/PP TPs

Sample	9	10	11	12	13	14	15	16
Ingredients	wt. %							
Exxon Bromobutyl 2244 Rubber	39.46		39.46		39.46		39.46	
Exxon Br-SBB-6755 Rubber	39.46		39.46		39.46		39.46	
Aristech TI 4007G Polypropylene	18.98							
Exxon PP7032 Polypropylene		18.98						
Lyondell 51 SU7A Polypropylene			18.98		18.98		18.98	
Aristech D008M Polypropylene				18.98		18.98	18.98	
Exxon Escorez 5320 Hydrocarbon	6.51	6.51	6.51		6.51		6.51	
Translink 37 Clay	1.89	1.89	1.89	1.89	1.89	1.89	1.89	1.89
Maglite D MgO	0.79	0.79	0.79	0.79	0.79	0.79	0.79	0.79
Stearic Acid F 1000	0.39	0.39	0.39	0.39	0.39	0.39	0.39	0.39
Irganox 3114	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
Ultranox 626	0.39	0.39	0.39	0.39	0.39	0.39	0.39	0.39
Exxon Parapol 950	25.37	25.37	25.37	25.37	25.37	25.37	25.37	25.37
ZnO	1.59	1.59	1.59	1.59	1.59	1.59	1.59	1.59
Aristech EP200F Polypropylene	2.84	2.84	2.84	2.84	2.84	2.84	2.84	2.84
Exxon Vistalon 808	0.71	0.71	0.71	0.71	0.71	0.71	0.71	0.71
DuPont HVA-2 (N,N-m-phenylene dimaleimide)	0.74	0.74	0.74	0.74	0.74	0.74	0.74	0.74
Lyondell ArcoPrims 350 White Oil	0.12	0.12	0.12	0.12	0.12	0.12	0.12	0.12
Total (%)	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Table 2 (continued)

Room Temperature Property

Sample	9	10	11	12	13	14	15	16
Specific Gravity (g/cm^3)	0.96	0.96	0.96	0.96	0.96	0.96	0.96	0.96
Hardness A, 5 sec.	74	74	74	74	77	77	80	80
EB, %	360	230	230	320	370	210	210	210
UTS, MPa (psi)	6.85 (1000)	7.58 (1100)	5.88 (850)	6.89 (1000)	8.98 (1300)	8.62 (1250)	7.58 (1100)	7.58 (1100)
Mod. (100, MPa (psi))	3.31 (480)	4.20 (610)	4.07 (590)	3.93 (570)	5.31 (770)	5.38 (780)	5.93 (860)	5.93 (860)
Tension Set, %	18	20	28	22	22	26	25	25
A.C.R. Viscosity, Pa·s (poise)								
204°C, 0.351 MPa (51 psi)	100 (1000)	80 (800)	50 (500)	40 (400)	88 (880)	70 (700)	83 (830)	58 (580)
Extrusion Surface Rating	132	54	72	54	120	69	107	69

EP 0 992 538 B1

[0056] In a third series of experiments a 1.6 l Banbury internal mixer was used as mixing device. Again, both star-branched halobutyls gave final products with higher tensile strength and elongation compared to the corresponding normal halobutyls.

[0057] Processability of finished products with star-branched polymers was significantly better vs. formulation with normal halobutyls. In fact, injection molded plates obtained from both star halobutyl based finished products, presented a smoother surface without flow marks compared to those based on normal halobutyls (sample 17 and 18 vs. control 1 and 2).

[0058] The quality of extrusion was much better (smoother) for both star halobutyl based product compared to normal halobutyl (sample 17 and 18 vs. control 1 and 2). The results are shown in the following Table 3:

Table 3

Sample	Control 1	17	18	Control
Ingredients	wt.%	wt.%	wt.%	wt.%
BB 2244	35.68			
MDB 90/4		35.68		
MDB 88/4			35.68	
CB 1068				35.68
PPH 1050	14.80	14.80	14.80	14.80
Neutral 600	34.50	34.50	34.50	34.50
Translink 37	1.99	1.99	1.99	1.99
SRF 762	2.00	2.00	2.00	2.00
Maglite D	0.45	0.45	0.45	0.45
Stearic Acid	0.45	0.45	0.45	0.45
Irganox 3114	0.10	0.10	0.10	0.10
Ultranox 626	0.18	0.18	0.18	0.18
ZnO	2.00	2.00	2.00	2.00
HVA-2	0.85	0.85	0.85	0.85
Unislip 1757	1.00	1.00	1.00	1.00
Vistalon 808	6.00	6.00	6.00	6.00
Total	100 %	100 %	100 %	100 %
Hardness Shore A 5, sec.	63	63	63	61
Direction 115 mm Mod 100, MPa	2.7	2.6	2.6	1.8
Mod 300, MPa		5.7		
EB %	277	307	200	130
UTS, MPa	5.5	5.9	4.3	3.1
Direction 85 mm Mod 100, MPa	2.4	2.3	2.3	2.4
Mod 300, MPa		5.3		
EB %	286	331	232	165
UTS, MPa	5.3	5.9	4.5	3.5
Tear (N/mm) direction 115 mm	25	24	24	20
direction 85 mm	23	23	22	20
Compression Set %				

EP 0 992 538 B1

Table 3 (continued)

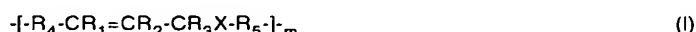
Sample	Control 1	17	18	Control
22 hrs, RT	28	29		
22 hrs, 70 °C	36	35		
Processability***				
Haake RPM 60				
Garvey Die				
Temp.				
170/190/200/190 °C				
Rating				
Surface	rough	smooth	smooth	very rough
Edge	rough	smooth	smooth	very rough
Lip	tearing	no tearing	no tearing	tearing
Injection Plate Surface	flow marks	no flow marks	no flow marks	a lot of flow marks

- [0059] The following typical procedures were used in carrying out the examples of this invention:
- [0060] The procedure to make samples 1 to 16 is illustrated by use of a Werner & Pfleiderer twin-screw extruder type ZSK-53. All of the plastic, rubber and other compounding ingredients except curing system are fed into the entry port of the extruder. In the first third of extruder, the composition is masticated to melt the plastic and to form an essentially homogeneous blend. Curing system is added through another entry port (vulcanization zone) located about one-third of the length of the barrel downstream from the initial entry port. A vent operating under reduced pressure is located near the outlet to remove any volatile by-products. Process oil and other additives are added at another entry port located about the middle of the vulcanization. The additives which could reduce the curing system activity like stabilizers are added downstream after vulcanization zone, close to outlet. Temperature set 170 °C (feeding zone), 175 °C, 180 °C, 190 °C, 200 °C (die zone). Final melt blend is pelletized under water.
- [0061] The samples 17, 18 and controls 1, 2 are made using an internal mixer type Banbury.
- [0062] Into a 1.6 l Banbury internal mixer using about 70 % of theoretical volume maintained at 160 °C, the rubber, thermoplastic, all the additives except ZnO, HVA-2 and process oil are added and mixed about 3 minutes keeping the temperature at about 180 to 200 °C. On third of process oil is added while continuing mixing for about another minute. Then the second third of the process oil is added while continuing to mix for another minute. Then curatives (ZnO, HVA-2) are added. After about 3 minutes mixing the last third of process oil is added. The mixed formulation was then discharged after two minutes of the last addition from the mixer and passed through a cold roll-mill to make a sheet. The sheet was ground into flakes and flakes were subsequently used for making plaques by injection molding or for extrusion processing.

40

Claims

1. A curable composition comprising a blend of
 - (i) a thermoplastic polyolefin resin; and
 - (ii) a curable star-branched rubber (copolymer).
2. The curable composition of claim 1 wherein the thermoplastic polyolefin resin is selected from homopolymers or copolymers of monoolefin monomers having from 2 to 7 carbon atoms.
3. The curable composition of claim 1 wherein the star-branched rubber is obtainable from the reaction of a C₄ to C₇ isomonoolefin and a C₄ to C₁₄ multiolefin with a branching agent.
4. The curable composition of claim 3 wherein the branching agent is represented by the following formulae (I) to (III):



EP 0 992 538 B1

wherein

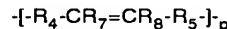
R₁, R₂ and R₃ independently represent hydrogen or a C₁ to C₁₅ alkyl group,
R₄ and R₅ independently represent a C₁ to C₁₅ alkylene group,
X represents halogen, and
m represents an integer of 4 to 100;



10

wherein

R₆ represents a C₁ to C₁₅ alkyl or an aryl group containing up to 14 carbon atoms,
R₄ and R₅ independently represent a C₁ to C₁₅ alkylene group,
X represents halogen, and
n represents an integer of 4 to 100;



20

wherein

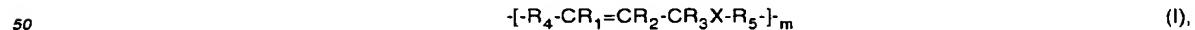
R₇ and R₈ independently represent hydrogen, a C₁ to C₁₅ alkyl group, an aryl group containing up to 14 carbon atoms or an C₂ to C₄ alkenyl group,
R₄ and R₅ independently represent a C₁ to C₁₅ alkylene group, and
p represents an integer of 7 to 1,000.

5. The curable composition of claims 3 or 4 comprising
 - 85 to 99.5% by weight of the C₄ to C₇ isomonoolefin, and
 - 0.5 to 15.0% by weight of the C₄ to C₁₄ multiolefin,based on the amount of isomonoolefin and multiolefin monomers.
- 30 6. The curable composition of claim 3 or 4 wherein the amount of the branching agent is between 0.5 and 5.0% by weight, based on the amount of the isomonoolefin and multiolefin monomers.
- 35 7. The curable composition of claim 1 wherein the star-branched rubber is a copolymer of isobutylene and isoprene including a branching agent.
- 40 8. The curable composition of claim 1 wherein the star-branched rubber is halogenated with chlorine, bromine or iodine.
- 45 9. The curable rubber composition of claim 8 wherein the star-branched rubber comprises between 0.05 and 5.0% by weight, based on said rubber, of chemically bound halogen.
10. The curable composition of claim 7 wherein the branching agent is selected from styrene-butadiene copolymers.
- 50 11. The curable composition of claim 1 comprising
 - 15 to 80 % by weight of the thermoplastic polyolefin resin (i), and
 - 85 to 20 % by weight of the star-branched rubber (ii),based on the total amount of (i) and (ii).
- 55 12. The curable composition of claim 1 further comprising a curative or curative system.

13. A thermoplastic elastomer vulcanizate obtainable from the curable composition as defined in any one of claims 1 to 12 by curing the rubber under conditions of shear at a temperature above the melting temperature of the thermoplastic component.
- 5 14. The thermoplastic elastomer vulcanizate of claim 13 wherein the star-branched rubber is partially or fully cured.
15. The thermoplastic elastomer vulcanizate of claim 13 comprising additives selected from reinforcing and non-reinforcing fillers plasticizers, antioxidants, stabilizers, compatibilizers, rubber processing oil, extender oils, lubricants, antblocking agents, antistatic agents, waxes, foaming agents, pigments, flame retardants and other conventional processing aids.
- 10 16. A method of preparing a thermoplastic elastomer vulcanizate from a curable composition comprising
(i) a thermoplastic polyolefin resin;
(ii) a curable star-branched rubber (copolymer); and
(iii) a curative for said rubber
by blending said curable composition under conditions of shear at a temperature above the melting temperature of the thermoplastic component.
- 20 17. The method of claim 16, wherein the curable rubber is partially or fully crosslinked.
18. A shaped article comprising a thermoplastic elastomer vulcanizate obtainable from a curable composition comprising a blend of
(i) a thermoplastic polyolefin resin; and
(ii) a curable star-branched rubber (copolymer),
by curing the rubber under conditions of shear at a temperature above the melting temperature of the thermoplastic component.
- 25 30

Patentansprüche

- 35 1. Härtbare Zusammensetzung, umfassend ein Blend aus
(i) einem thermoplastischen Polyolefinharz und
(ii) einem härbaren, sternförmig verzweigten Kautschuk (Copolymer).
- 40 2. Härtbare Zusammensetzung gemäß Anspruch 1, in welcher das thermoplastische Polyolefinharz aus Homopolymeren oder Copolymeren von Monoolefin-Monomeren mit 2 bis 7 Kohlenstoffatomen ausgewählt ist.
3. Härtbare Zusammensetzung gemäß Anspruch 1, in welcher der sternförmig verzweigte Kautschuk durch die Umsetzung eines C₄-C₇-Isomonoolefins und eines C₄-C₁₄-Multiolefins mit einem Verzweigungsmittel erhältlich ist.
- 45 4. Härtbare Zusammensetzung gemäß Anspruch 3, in welcher das Verzweigungsmittel durch die folgenden Formeln (I) bis (III) dargestellt wird:



wobei

55 R₁, R₂ und R₃ unabhängig voneinander Wasserstoff oder eine C₁-C₁₅-Alkylgruppe darstellen,
R₄ und R₅ unabhängig voneinander eine C₁-C₁₅-Alkylengruppe darstellen,
X Halogen darstellt, und
m eine ganze Zahl von 4 bis 100 darstellt;

EP 0 992 538 B1

$[-R_4-CR_6X-R_5-]_n$

(II),

wobei

5

R_6 eine C_1-C_{15} -Alkylgruppe oder eine Arylgruppe mit bis zu 14 Kohlenstoffatomen darstellt,
 R_4 und R_5 unabhängig voneinander eine C_1-C_{15} -Alkylengruppe darstellen,
 X Halogen darstellt und
 n eine ganze Zahl von 4 bis 100 darstellt;

10

$[-R_4-CR_7=CR_8-R_5-]_p$

(III)

wobei

15

R_7 und R_8 unabhängig voneinander Wasserstoff, eine C_1-C_{15} -Alkylgruppe, eine Arylgruppe mit bis zu 14 Kohlenstoffatomen oder eine C_2-C_4 -Alkenylgruppe darstellen,
 R_4 und R_5 unabhängig voneinander eine C_1-C_{15} -Alkylengruppe darstellen, und
 p eine ganze Zahl von 7 bis 1000 darstellt.

20

5. Härtbare Zusammensetzung gemäß den Ansprüchen 3 oder 4, umfassend

- 85 bis 99,5 Gew.-% des C_4-C_7 -Isomonoolefins und
- 0,5 bis 15,0 Gew.-% des C_4-C_{14} -Multiolen,

25

bezogen auf die Menge der Isomonoolein- und Multiolen-Monomere.

30

6. Härtbare Zusammensetzung gemäß den Ansprüchen 3 oder 4, in welcher die Menge des Verzweigungsmittels zwischen 0,5 und 5,0 Gew.-% liegt, bezogen auf die Menge der Isomonoolein- und Multiolen-Monomere.

35

7. Härtbare Zusammensetzung gemäß Anspruch 1, in welcher der sternförmig verzweigte Kautschuk ein Copolymer von Isobutylen und Isopren ist und ein Verzweigungsmittel einschließt.

40

8. Härtbare Zusammensetzung gemäß Anspruch 1, in welcher der sternförmig verzweigte Kautschuk mit Chlor, Brom oder Iod halogeniert ist.

9. Härtbare Zusammensetzung gemäß Anspruch 8, in welcher der sternförmig verzweigte Kautschuk zwischen 0,05 und 5,0 Gew.-%, bezogen auf den Kautschuk, chemisch gebundenes Halogen umfasst.

45

10. Härtbare Zusammensetzung gemäß Anspruch 7, in welcher das Verzweigungsmittel aus Styrol-Butadien-Copolymeren ausgewählt ist.

11. Härtbare Zusammensetzung gemäß Anspruch 1, umfassend

50

- 15 bis 80 Gew.-% des thermoplastischen Polyolefinharzes (i) und
- 85 bis 20 Gew.-% des sternförmig verzweigten Kautschuks (ii), bezogen auf die Gesamtmenge von (i) und (ii).

12. Härtbare Zusammensetzung gemäß Anspruch 1, die weiterhin ein Härtungsmittel oder ein Härtungssystem umfasst.

55

13. Thermoplastisches Elastomer-Vulkanisat, das aus der härbaren Zusammensetzung gemäß irgendeinem der Ansprüche 1 bis 12 durch Härteten des Kautschuks unter Scherbedingungen bei einer Temperatur oberhalb der Schmelztemperatur der thermoplastischen Komponente erhältlich ist.

55

14. Thermoplastisches Elastomer-Vulkanisat gemäß Anspruch 13, in welchem der sternförmig verzweigte Kautschuk teilweise oder vollständig gehärtet ist.

15. Thermoplastisches Elastomer-Vulkanisat gemäß Anspruch 13, welches Additive umfasst, die aus verstärkenden und nicht verstärkenden Füllstoffen, Weichmachern, Antioxidationsmitteln, Stabilisatoren, Kompatibilisierungsmitteln, Kautschuk-Verarbeitungölen, Extenderölen, Gleitmitteln, Antiblockierungsmitteln, antistatischen Mitteln, Wachsen, Verschäumungsmitteln, Pigmenten, Flammverzögerungsmitteln und anderen herkömmlichen Verfahrenshilfsmitteln ausgewählt sind.
- 5
16. Verfahren zur Herstellung eines thermoplastischen Elastomer-Vulkanisats aus einer härtbaren Zusammensetzung, umfassend
- 10 (i) ein thermoplastisches Polyolefinharz;
(ii) einen härtbaren, sternförmig verzweigten Kautschuk (Copolymer) und
(iii) ein Härtungsmittel für den Kautschuk,
- 15 durch Vermischen der härtbaren Zusammensetzung unter Scherbedingungen und bei einer Temperatur oberhalb der Schmelztemperatur der thermoplastischen Komponente.
17. Verfahren gemäß Anspruch 16, wobei der härtbare Kautschuk teilweise oder vollständig vernetzt ist.
18. Geformter Gegenstand, umfassend ein thermoplastisches Elastomer-Vulkanisat, das aus einer härtbaren Zusammensetzung, umfassend ein Blend aus
- 20 (i) einem thermoplastischen Polyolefinharz; und
(ii) einem härtbaren, sternförmig verzweigten Kautschuk (Copolymer);
- 25 durch Härt(en) des Kautschuks unter Scherbedingungen und bei einer Temperatur oberhalb der Schmelztemperatur der thermoplastischen Komponente erhältlich ist.

Revendications

- 30 1. Composition vulcanisable comprenant un mélange de
- (i) une résine de polyoléfine thermoplastique, et
(ii) un caoutchouc (copolymère) ramifié en étoile vulcanisable.
- 35 2. Composition vulcanisable selon la revendication 1, dans laquelle la résine de polyoléfine thermoplastique est choisie parmi des homopolymères ou des copolymères de monomères mono-oléfiniques comportant de 2 à 7 atomes de carbone.
- 40 3. Composition vulcanisable selon la revendication 1, dans laquelle le caoutchouc ramifié en étoile peut être obtenu à partir de la réaction d'une isomono-oléfine en C₄ à C₇ et d'une multi-oléfine en C₄ à C₁₄ avec un agent de ramifications.
- 45 4. Composition vulcanisable selon la revendication 3, dans laquelle l'agent de ramification est représenté par les formules (I) à (III) suivantes :



50 dans laquelle

R₁, R₂ et R₃ représentent indépendamment un atome d'hydrogène ou un groupement alkyle en C₁ à C₁₅,
R₄ et R₅ représentent indépendamment un groupement alkylène en C₁ à C₁₅,
X représente un atome d'halogène, et
m représente un nombre entier de 4 à 100,

$[-R_4-CR_6X-R_5-]_n$

(II)

dans laquelle

5

R_6 représente un groupement alkyle en C_1 à C_{15} ou un groupement aryle contenant jusqu'à 14 atomes de carbone,

R_4 et R_5 représentent indépendamment un groupement alkylène en C_1 à C_{15} ,

X représente un atome d'halogène, et

10

n représente un nombre entier de 4 à 100,

 $[-R_4-CR_7=CR_8-R_5-]_p$

(III)

15

R_7 et R_8 représentent indépendamment un atome d'hydrogène, un groupement alkyle en C_1 à C_{15} , un groupement aryle contenant jusqu'à 14 atomes de carbone ou un groupement alcényle en C_2 à C_4 ,

R_4 et R_5 représentent indépendamment un groupement alkylène en C_1 à C_{15} , et

p représente un nombre entier de 7 à 1 000.

20

5. Composition vulcanisable selon la revendication 3 ou 4, comprenant

- 85 à 99,5 % en poids de l'isomono-oléfine en C_4 à C_7 , et
- 0,5 à 15,0 % en poids de multi-oléfine en C_4 à C_{14} ,

25

sur la base de la quantité des monomères d'isomono-oléfine et de multi-oléfine.

6. Composition vulcanisable selon la revendication 3 ou 4, dans laquelle la proportion de l'agent de ramification se situe entre 0,5 et 5,0 % en poids, sur la base de la quantité des monomères d'isomono-oléfine et de multi-oléfine.

30

7. Composition vulcanisable selon la revendication 1, dans laquelle le caoutchouc ramifié en étoile est un copolymère d'isobutylène et d'isoprène comprenant un agent de ramification.

8. Composition vulcanisable selon la revendication 1, dans laquelle le caoutchouc ramifié en étoile est halogéné avec du chlore, du brome ou de l'iode.

35

9. Composition de caoutchouc vulcanisable selon la revendication 8, dans laquelle le caoutchouc ramifié en étoile comprend entre 0,05 et 5,0 % en poids, sur la base dudit caoutchouc, d'halogène lié chimiquement.

40

10. Composition vulcanisable selon la revendication 7, dans laquelle l'agent de ramification est choisi parmi des copolymères styrène-butadiène.

11. Composition vulcanisable selon la revendication 1, comprenant

- 15 à 80 % en poids de la résine de polyoléfine thermoplastique (i), et
- 85 à 20 % en poids du caoutchouc ramifié en étoile (ii),

sur la base de la quantité totale de (i) plus (ii).

50

12. Composition vulcanisable selon la revendication 1, comprenant en outre un vulcanisant ou un système vulcanisant.

13. Vulcanisé d'élastomère thermoplastique pouvant être obtenu à partir de la composition vulcanisable telle que définie dans l'une quelconque des revendications 1 à 12, en vulcanisant le caoutchouc dans des conditions de cisaillement à une certaine température au-dessus de la température de fusion du composant thermoplastique.

55

14. Vulcanisé d'élastomère thermoplastique selon la revendication 13, dans lequel le caoutchouc ramifié en étoile est partiellement ou totalement vulcanisé.

15. Vulcanisat d'élastomère thermoplastique selon la revendication 13, comprenant des additifs qui sont choisis parmi des agents de remplissage plastifiants de renforcement et de non-renforcement, des antioxydants, des stabilisants, des agents de compatibilité, une huile de traitement du caoutchouc, des huiles d'extenseurs, des lubrifiants, des agents antiadhérents, des agents antistatiques, des cires, des agents moussants, des pigments, des ignifuges ainsi que d'autres adjuvants de fabrication classiques.

5 16. Procédé de préparation d'un vulcanisat d'élastomère thermoplastique à partir d'une composition vulcanisable comprenant

- 10 (i) une résine de polyoléfine thermoplastique,
 (ii) un caoutchouc (copolymère) ramifié en étoile vulcanisable, et
 (iii) un vulcanisant pour ledit caoutchouc

15 en mélangeant ladite composition vulcanisable dans des conditions de cisaillement à une certaine température au-dessus de la température de fusion du composant thermoplastique.

17. Procédé selon la revendication 16, dans lequel le caoutchouc vulcanisable est partiellement ou totalement réticulé.

20 18. Article façonné comprènant un vulcanisat d'élastomère thermoplastique pouvant être obtenu à partir d'une composition vulcanisable comprenant un mélange de

- 25 (i) une résine de polyoléfine thermoplastique, et
 (ii) un caoutchouc (copolymère) ramifié en étoile vulcanisable,

en vulcanisant le caoutchouc dans des conditions de cisaillement à une certaine température au-dessus de la température de fusion du composant thermoplastique.

30

35

40

45

50

55